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Influence of the discharge mode on the optical and passivation properties of SiN_x:H deposited by PECVD at atmospheric pressure

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Abstract

The cost of industrial silicon solar cells could be greatly reduced by the implementation of PECVD at atmospheric pressure for the deposition of the silicon nitride (SiN) antireflective coating. For a successful development of this vacuum-free process tool, a deep understanding of the plasma discharge mode has to be undertaken. This work focuses on the control of a wide range of plasma excitation conditions in order to obtain homogeneous dielectric barrier discharges (DBD) at atmospheric pressure, and thus dense and uniform SiN layers. The influence of the discharge mode is then studied in order to optimize the optical and passivation properties of the SiN thin films, showing good antireflective properties as well as surface recombination velocities as low as 15 $cm.s^{-1}$.

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Keywords: silicon nitride; antireflective and passivation coating; atmospheric pressure discharges; dielectric barrier discharge (DBD)

1. Introduction

The hydrogenated silicon nitride SiN_x:H (SiN in the following) antireflective coating of silicon solar cells is currently deposited by low pressure plasma-enhanced chemical vapour deposition (LP-PECVD). The major advantage of SiN films is that they provide both an adequate antireflective behavior and efficient surface and bulk passivation properties [1,2]. The promising alternative deposition tool explored in this work is based on direct

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atmospheric pressure plasma (AP-PECVD) using a homogeneous dielectric barrier discharge (DBD) in $Ar/SiH_4/NH_3$ gas mixture [3]. Such process can contribute to reduce the production cost of silicon solar cells by avoiding the need for expensive vacuum equipments as well as it could improve the solar cell production throughput and yield, such a process being compatible with a fully in-line fabrication process [4]. The lab-scale AP-PECVD reactor developed in our laboratory allows to adjust the discharge mode over a wide range of frequencies, providing a unique tool for the study of the influence of such plasma sources on the final optical and passivation properties of the deposited SiN thin films, and thus giving a deep understanding to better optimize the SiN antireflective and passivation layer.

2. Experimental

Fig. 1 shows a schematic view of the AP-PECVD discharge cell which is composed of two high-voltage (HV) electrodes that can generate two 14×50 mm² discharge zones. Each electrode was realized by metallizing one of the inner sides of an alumina (Al_2O_3) square tube with 3 mm thick walls and rounded-off corners. The ground electrode is at the opposite side of the 1 mm gas gap with a larger metallized surface on the rear face of an alumina plate. This configuration is widely used in industrial scale reactors for roll-to-roll corona treatment [5]. The gas mixture ($Ar + NH_3 + SiH_4$) was injected between the two dielectric square bars and the total pressure was kept at 1 bar during all the processes. The gas mixture was composed of ammonia (NH_3) and silane (SiH_4) as reactive gases, and argon (Ar) as dilution gas, while substrate heating was fixed at 400°C. The precursor concentrations were adjusted to a few hundreds ppm while dilution gas flow was a few liters per minute. The ammonia-to-silane gas flow ratio $R = NH_3/SiH_4$ was adjusted between 1 and 4 in order to obtain different SiN stoichiometries.

In the static mode, only the parts which interact directly with the plasma were coated. To obtain homogenous coatings over all the surface of the samples, a translation system moved the sample holder back and forth with a defined speed (100 mm/min - dynamic mode). Deflectors were added to the dielectric bars in order to avoid powder formation and to decrease the light absorption (extinction coefficient *k*) within SiN thin films [6].

The plasma excitation conditions were widely varied in order to study their impact on the final SiN layer properties. Sinusoidal voltage waveforms were used with frequency varying between 50 kHz and 9.6 MHz thanks to homemade electrical circuits [7]. The excitation was eventually modulated by adding a square signal with a period of 5 ms (200Hz) and a variable duty cycle $DC=T_{on}/(T_{on}+T_{off})$. In addition, a repetitive nanopulsed power supply was also tested using a FID III (FPG20-30MkS50) generator to make high voltage pulses between 5 and 50 ns with a repetitive rate between 1 and 30 kHz.

The discharge was characterized using a combination of electrical and optical measurements. In particular, discharge modes were determined using an intensified CCD camera (Princeton Instruments PI-MAX II) synchronized to the applied voltage, with a lens working in the UV-Visible range and an exposure time as short as 5 ns.

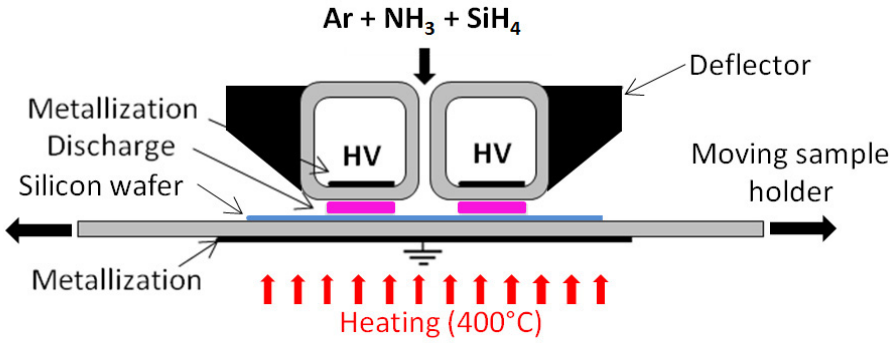

Fig. 1. Schematic view of the AP-PECVD discharge cell.

The SiN layer thickness and optical properties were determined by spectroscopic ellipsometry measurements (Jobin-Yvon MM-16), while the chemical composition was studied by Fourier Transform Infra-Red spectroscopy (Nicolet 6700 FTIR) in transmission mode. The SiN surface passivation properties were obtained using a Sinton WCT-120 lifetime tester to characterize SiN coated Float Zone (FZ) silicon wafers.

3. Results and discussion

3.1. Plasma sources

Different discharges modes are obtained in function of the voltage frequency. Glow and Townsend dielectric barrier discharges (GDBD and TDBD, respectively) are obtained over low frequency range (50 - 550 kHz) while radiofrequency dielectric barrier discharge (RF-DBD) appear from 3 MHz [7]. Typical current discharge curves during one excitation cycle of Glow and RF-DBD are shown in Fig. 2, along with the power supply voltage and the plasma light normalized to its maximum. A clear difference between this two discharge modes is that the plasma is always turned on for RF-DBD while it is off during 90% of the period for Glow DBD, because of a larger time for charge accumulation on the dielectric bars which induces a voltage opposite to the voltage applied on the gas, consequently turning off the discharge. Furthermore, the measured RF current discharge is two order of magnitude higher than the GDBD one whereas the applied voltage is 5 to 10 times lower. On the other hand, nanosecond repetitive pulsed (NRP) DBD is a pulsed plasma with plasma light turned on during approximately the time of the voltage pulse (5-20 ns) but with a very long exponential decay (characteristic time ~450 ns close to the GDBD decay time ~750 ns). This large decay time can be explained by a high light intensity (10-fold that of GDBD) combined with a huge discharge current (30-fold that of GDBD) and a high applied voltage (3kV), which induce the creation of a massive concentration of excited states of Ar that need a much longer time to de-excite. These large differences in the plasma physical characteristics are expected to lead to strong disparities in chemical reactions within the plasma and at the silicon substrate surface, and consequently in the final properties of the deposited SiN layers.

In order to obtain a dense and uniform SiN layer, the discharge should be homogeneous at the time scale of the process and the first step was to find the conditions leading to a homogeneous DBD. Then, Glow, Townsend, radiofrequency along with nanosecond repetitive pulsed DBD were compared according to their working domain and power, using the same reactor configuration. Fig. 3-a shows the maximum power of the different homogeneous DBD obtained with the experimental conditions of this study, as a function of the frequency for sinusoidal voltage waveforms and according to the repetition rate for nanopulsed voltage. The breakdown voltage is also shown to illustrate the differences between the numerous studied discharges. At first glance, higher is the voltage higher is the

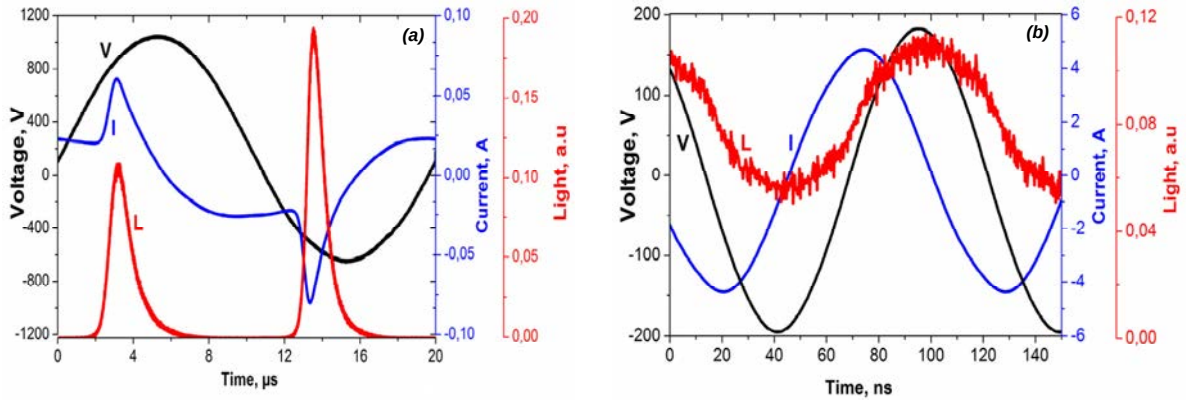

Fig. 2. Power supply voltage (V) and discharge current (I) as a function of time during one excitation cycle for (a) Glow DBD (50kHz) and (b) RF-DBD (9.1MHz) in Argon. Normalized plasma light intensity (L) variation is also shown for both cases.

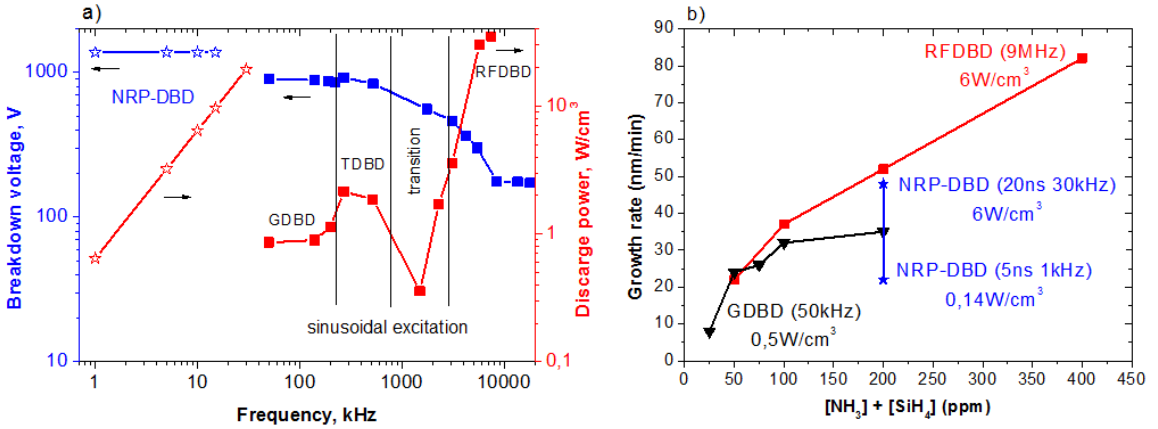

Fig. 3. (a) AP-PECVD breakdown voltage and maximum power density as a function of frequency. (b) AP-PECVD deposition velocity of SiN as a function of total precursor concentration with R=[NH_3]/[SiH_4]=2 for different discharges modes

electron energy. The largest power associated with a homogeneous discharge in Ar/NH_3/SiH_4 is obtained with RF-DBD (36 W.cm^{-3}). NRP-DBD also leads to a high discharge power of 19 W.cm^{-3} but involves a breakdown voltage 7 times higher than for RF-DBD. On the other hand, GDBD leads to much lower power densities of 1 W.cm^{-3} or less, limiting the energetic species density and therefore the deposition velocity.

Fig. 3-b shows the SiN deposition velocity according to the total precursor concentration ([NH_3]+[SiH_4]). At constant discharge power (0.5 W.cm^{-3}), the GDBD deposition velocity saturates around 30 nm.min^{-1} with increasing precursor concentration. On the other hand, RF-DBD allows to reach higher power discharges and the corresponding deposition velocity increases almost linearly with the total precursor concentration. The highest deposition velocity is reached with a precursor concentration of 400 ppm (80 nm.min^{-1}). For a same power density (6 W.cm^{-3}), similar deposition velocities are obtained applying RF- and NRP-DBD. Besides, if the power of NRP-DBD is kept lower than that of GDBD, the deposition velocity is also lower. Therefore, for a fixed precursor concentration, the deposition velocity appears to be controlled by the discharge power rather than the electron energy, density or kinetics. The latter are likely to be controlled by the voltage amplitude and waveform.

3.2. Optical and conformity properties

Fig. 4 shows the evolution of the SiN refractive index according to the ammonia-to-silane gas flow ratio R = NH_3/SiH_4 for different plasma sources and reactors. Results are presented for three different homogeneous DBD's (GDBD, RF-DBD, NRP-DBD) in Ar/NH_3/SiH_4 as well as for two different low pressure plasma reactors using either low frequency (40 kHz) in NH_3/SiH_4 or microwave (2.45 GHz) in Ar/NH_3/SiH_4 discharges. All SiN films were obtained at 400°C.

Whatever the plasma conditions, the refractive index of atmospheric pressure grown SiN films is easily varied in a large range, from n = 1.83 to n = 2.4. The lower is the ratio R = NH_3/SiH_4, the higher is the refractive index. This result is explained by the relationship between the refractive index and the Si/N ratio in the coating: the refractive index increases proportionally with the silicon content of the film [2].

The NH_3/SiH_4 ratio that produces SiN films with a given refractive index depends on the plasma source and the dilution gas. The low pressure plasma without argon as dilution gas leads to SiN stoichiometries clearly different from the four other configurations. In this case, a much higher proportion of NH_3 is necessary to get the desired refractive index showing that more ammonia is necessary to obtain the same Si/N ratio in the coating. The effect of adding argon to the gas mixture seems to modify the ammonia ionization and dissociation process to a great extent. Ar-NH_3 being a Penning mixture, this could be related to the efficient energy transfer from argon metastables to ammonia leading to radicals and ions. For low pressure plasma, argon may also have influence on the electron energy distribution.

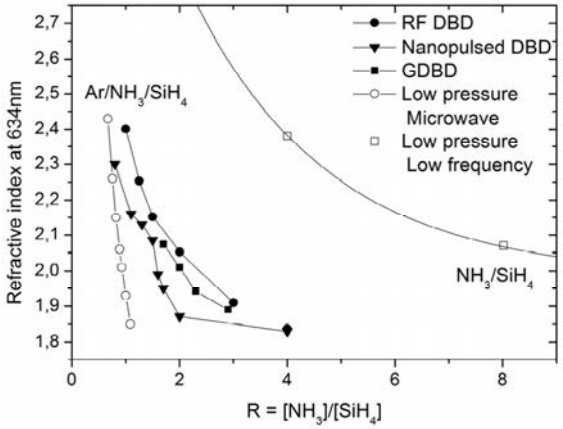

Fig. 4. SiN refractive index as a function of R=NH3/SiH4 for different discharges modes.

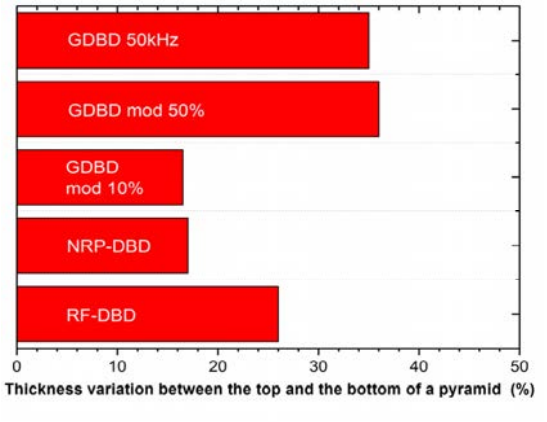

Fig. 5. SiN coating conformity on KOH textured silicon samples.

At atmospheric pressure, the SiN refractive index is slightly but significantly dependent on the voltage waveform: for a given refractive index, a higher NH_3 concentration is needed for RF-DBD than for GBDB. For NRP-DBD (5 ns pulse width with 1 kHz repetition rate), even less ammonia is needed to obtain the same refractive index. This can be related to the difference in NH_3^+ flow to the surface. In an Ar-NH_3 discharge at atmospheric pressure, Ar^+ are rapidly converted in Ar_2^+ (τ = 140 ns) by a three-body reaction. Then, as the charge transfer between Ar_2^+ and NH_3 is efficient (τ = 700 ns), NH_3^+ is the dominant ion in the plasma. However, in RF-DBD, the metastable density should be low. Moreover, ions are confined in the gas bulk and their contribution to the surface chemistry is low compared to the case of GDBD where they actively participate in the discharge development. On the other hand, the NRP-DBD is unipolar and the substrate is on the cathode, so the flux of NH_3^+ should be rather high. This is confirmed by the increase of the refractive index, for the same NH_3/SiH_4 value, when the substrate is on the anode.

To avoid significant light absorption within the silicon nitride film, the gas flow ratio R was adjusted thereafter to obtain SiN layers with refractive index equal to 2.1, which corresponds to a negligible extinction coefficient k, suitable to act as antireflective coating of silicon solar cells. The minimization of the extinction coefficient led to the optimization of the reactor configuration, which has been detailed elsewhere [6].

A drawback of PECVD at atmospheric pressure is that the mean free path of radicals in the plasma is very small (< 1 µm) compared to deposition at low pressure. This factor can explain the lack of coating conformity observed on textured silicon surfaces: the thickness of the SiN film is thicker on the top than on the bottom of the pyramid. The higher is the pyramid the larger is the difference, which can be related to the high reactivity of SiH_4 radicals. Fig. 5 illustrates the thickness variation between the top and the bottom of pyramids obtained by KOH texturization of multicrystalline silicon samples. The values were averaged for numerous pyramids observed by Scanning Electron Microscope (SEM). These results show that the film conformity is pretty bad for GDBD and RF-DBD leading to poor reflectivity properties for antireflective purpose. Indeed, the resulting reflectivity of a GDBD (50kHz) SiN film deposited on textured silicon is shown in Fig. 6-a: the effective reflectivity of the SiN film deposited by AP-PECVD is 0.8% higher than an equivalent SiN layer deposited by LP-PECVD. As the transmitted light to the silicon substrate is directly proportional to the short-circuit current density J_{sc} of the solar cell, such antireflective coating would induce a significant current loss and consequently a reduced solar cell efficiency. It has been checked by µAuger analysis that the film chemical composition is similar on the top and on the bottom of the pyramids and thus the thickness anisotropy is believed to be the cause of the differences observed between the reflectivity curves (Fig. 6-a). Indeed, the gradual thickness variation of the SiN coating leads to a combination of distinct reflectivity curves averaged at the macroscopic scale, as illustrated by Fig. 6-b. This figure shows the effect of the SiN thickness on the

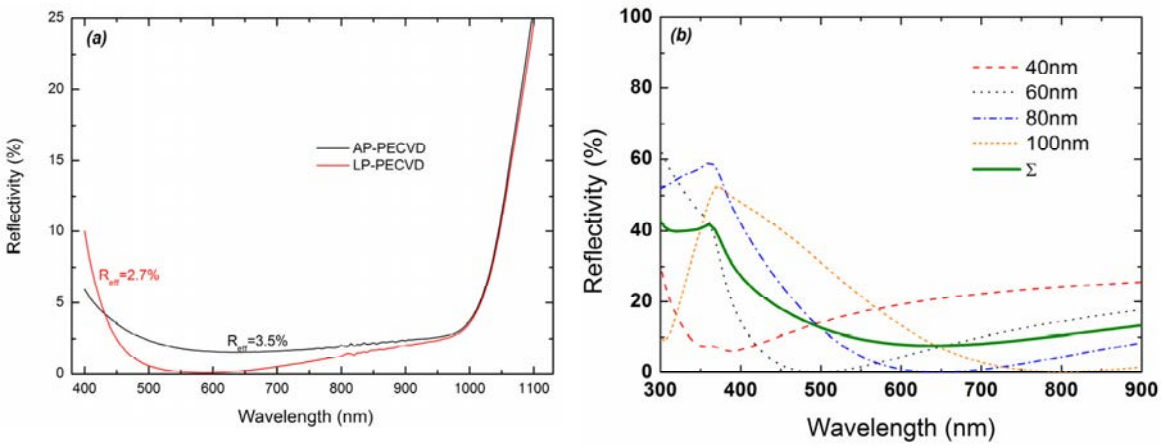

Fig. 6. (a) Reflectivity measurements performed on textured wafers coated by either LP- and AP-PECVD SiN films. (b) Simulated reflectivity curves according to the thickness of SiN films deposited on polished silicon wafers. The thick green curve is the arithmetic sum of the reflectivity of SiN/Si structures with different SiN thicknesses (average SiN thickness of 70nm).

SiN/Si reflectivity curve and demonstrates that the averaged sum of these curves leads to a global reflectivity which is is not zeroed for any wavelength.

The film conformity is much improved reaching acceptable values when using NRP-DBD (Fig. 5), which can be related to a high density of radicals combined with a larger time for surface reaction as such plasma is a pulsed one with a very short duty cycle around DC=0.1%. This is supported by the results obtained with 200Hz modulated GDBD which show that for a short duty cycle (DC=10%), the modulation of the plasma with a square signal significantly reduces the thickness gradient. Reactive species are created when the plasma is turned on and surface reaction are subsequently favored when the plasma is turned off. The duty cycle should be lower than 50% in order to leave time for surface reaction otherwise film conformity is not improved by modulation. Furthermore, the drawback of low deposition velocity is avoided by increasing the discharge power [8].

3.3. Chemical properties

FTIR absorption spectra were measured on SiN films deposited with different homogeneous DBD modes, giving insight into the chemical bonds involved in the thin SiN films. In particular, hydrogen bonds were studied through the Si-H stretching band around 2180 cm^{-1} and the N-H stretching band around 3330 cm^{-1}. The area of these infrared bands, normalized to the film thickness, can give a relative estimate of the Si-H and N-H bond densities as well as rough relative measure of the hydrogen concentration within the layer [2]. Fig. 7 shows the results for different DBD modes at atmospheric pressure and compared to values obtained with a standard low pressure PECVD SiN layer.

A clear difference between SiN layers obtained by low and atmospheric pressure PECVD is the total hydrogen content within the thin film: the hydrogen concentration is much higher in the case of AP-PECVD, revealing differences in film density. Indeed, the high hydrogen content of RF-DBD SiN layers is likely to induce a low film density. On the other hand, GDBD SiN films show a high hydrogen content but should be relatively stable upon annealing as a larger part of its hydrogen is bonded to nitrogen atoms, N-H bonds being stronger than Si-H bonds [2]. Furthermore, NRP-DBD SiN layers have the chemical properties the closest to those of low pressure SiN films which indicate a relative higher density and stability of these SiN layers.

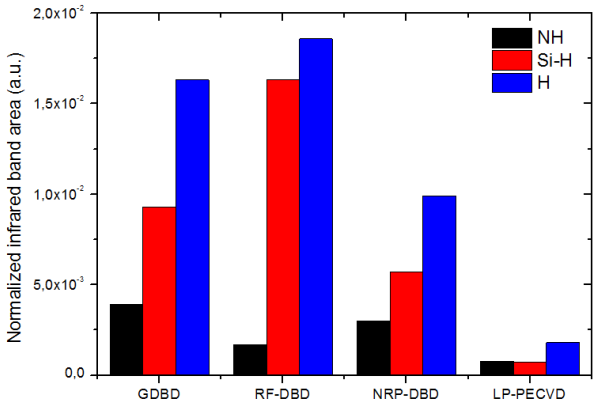

Fig. 7. FTIR N-H and Si-H band area normalized to the film thickness for different AP-PECVD discharge modes and compared to Low Pressure PECVD SiN films. Rough estimate of the hydrogen content is also shown for comparison.

3.4. Passivation properties

The passivation properties of SiN deposited by AP-PECVD were studied according to the different discharges modes. Additionally, a square-wave modulation (200 Hz - DC = 30%) was applied to the Glow mode giving SiN film with the best results. Moreover, in order to simulate the influence of the last fabrication step of silicon solar cell, the effect of rapid thermal annealing (RTA - 790°C during 1 s) was also analyzed.

Fig. 8 shows the lifetime results, indicating that for all plasma sources studied, AP-PECVD SiN films provide reasonable surface passivation properties before annealing. Low frequency (GDBD and TDBD) samples lead to roughly the same value of 200-250 µs whereas the passivation provided by RF-DBD is less efficient (130 µs). The highest lifetime value is obtained with NRP-DBD reaching 340 µs which corresponds to a low surface recombination velocity of S = 44 cm.s^{-1}. These results can be explained by a higher film density for such films, as previously suggested by FTIR measurements, leading to a better neutralization of surface defects.

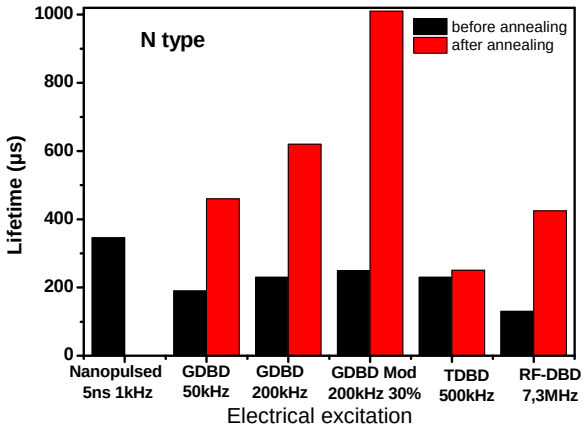

Fig. 8. Minority charge carrier effective lifetime τ_{eff} as a function of the plasma excitation (n-type FZ Si), before and after RTA

After annealing, the surface passivation quality is greatly improved for all the samples, except for the Townsend discharge. This can be related to the stability of the refractive index after annealing, whatever the plasma source: such result indicates a dense layer with good chemical stability. Moreover, SiN films deposited with a modulated 200 kHz plasma frequency lead to the outstanding value of τ_{eff} = 1 ms after RTA, corresponding to a surface recombination velocity of S=15 cm.s^{-1}. The large enhancement of the surface passivation when using a modulated plasma is explained by a significant improvement of the chemistry uniformity correlated to the better conformity of these SiN films, as previously described.

4. Conclusion

This work shows that it is possible to adjust the AP-PECVD reactor discharge mode in order to optimize the optical and passivation properties of SiN thin films and thus to obtain efficient antireflective coating for silicon solar cells at low cost. The different plasma sources lead to different discharge power densities which are believed to control the deposition velocity for a fixed precursor concentration. NRP-DBD and RF-DBD allow to reach higher power densities than low frequency GDBD and lead to high deposition velocity (up to 80 nm.min^{-1}). SiN films with optimum optical properties for antireflective coating purpose are obtained whatever the plasma source. Acceptable film conformity and very good surface passivation results are obtained with nanopulsed repetitive DBD and modulated Glow DBD, showing that the complex challenge of depositing uniform and dense SiN layers by plasma at atmospheric pressure can be tackled by optimizing the discharge mode and finding the balance between radical dissociation and surface reaction.

Acknowledgements

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References

[1] Cuevas A, Kerr MJ, Schmidt J. Passivation of crystalline silicon using silicon nitride. WCPEC-3, Osaka, Japan, (May 2003).
[2] Lelièvre J-F, Fourmond E, Kaminski A, Palais O, Ballutaud D and Lemiti M. Study of the composition of hydrogenated silicon nitride SiN_x:H for efficient surface and bulk passivation of silicon. Solar Energy Materials and Solar Cells 2009; 93: 1281.
[3] Massines F, Sarra-Bournet C, Fanelli F, Naude N and Gherardi N. Atmospheric Pressure Low Temperature Direct Plasma Technology: Status and Challenges for Thin Film Deposition. Plasma Processes and Polymers 2012; 9: 1041-1073.
[4] Kakiuchi H, Ohmi H and Yasutake K. Atmospheric-pressure low-temperature plasma processes for thin film deposition. Journal of Vacuum Science and Technology A 2014; 32: 030801.
[5] Starostin SA, Premkumar PA, Creatore M, Veldhuizen EM, Vries H, Paffen RMJ, Sanden MCM. On the formation mechanisms of the diffuse atmospheric pressure dielectric barrier discharge in CVD processes of thin silica-like films. Plasma Sources Science and Technolgy 2009; 18(4): 045021.
[6] Vallade J, Pouliquen S, Lecouvreur P, Bazinette R, Hernandez E, Quoizola S, Massines F. a-SiNx:H antireflective and passivation layer deposited by atmospheric pressure plasma. Energy Procedia 2012; 27:365-371.
[7] Bazinette R, Subileau R, Paillol J, Massines F. Identification of the different diffuse dielectric barrier discharges obtained from 50kHz to 9MHz in Ar/NH_3 at atmospheric pressure. Plasma Sources Science and Technology 2014; 23: 035008.
[8] Vallade J, Bazinette R, Gaudy L and Massines F. Effect of glow DBD modulation on gas and thin film chemical composition: Case of Ar/SiH4/NH3 mixture. Journal of Phyics D: Applied Physics 2014; 47(22): 224006.